中空粒子構造を利用したナノ粒子空間分布の可逆的制御

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論文内容要約

Background and objectives of the present work are described in Chapter 1. Particles smaller than 100 nm, which are called “nanoparticles,” exhibit physical and chemical properties different from bulk materials. To expand the potential of the nanomaterials, it is required to programmably create assemblies of NPs in a limited space. The specific properties of NPs can be effectively utilized in locally condensed areas in the particle assembly. Some researchers indicated that the condensed states of NPs exhibit interesting phenomena different from the dispersed states of NPs, for instance, light trapping in solar cells and photocatalysts, and optical magnetism in metamaterials. Plasmonic nanoparticles (NPs) such as silver and gold are well known as materials having unique properties (e.g. catalytic, magnetic, optical, and sensing properties). Oscillation of the NP free electrons induced by light irradiation generates a local electric field on the NP surface, resulting in unique properties of the NPs. Irradiation light with a specific wavelength is absorbed by the NPs, which is a typical phenomenon of plamsmonic NPs called Localized Surface Plasmon Resonance (LSPR). Surface-enhanced Raman scattering (SERS) has received enormous interest since it was discovered in the 1970s because strong Raman intensities are obtained from molecules neighboring the NP surfaces. In the case of plasmonic NPs, creation of hotspots at which the electric field is enhanced by assembling the NPs can be a practical way to improve the plasmoinc properties.

Approaches to control over the spatial distribution of micron- or submicron-sized particles have been reported by many researchers. However, rapid aggregation in the process of assembling generally accompanies irreversible agglomeration of the NPs, causing a deterioration of intrinsic properties depending on particle sizes. Nano-sized particles, in particular, tend to be more easily aggregated than submicron- or larger-sized particles because of the low colloidal stability of NPs. Based on the background, the goal of the present work is development of a new system for reversible control over the spatial distribution of gold (Au) NPs in a liquid phase. In this thesis, the spatial distribution of the NPs is defined as the assembled or dispersed states of the NPs. We have focused on the hollow silica (SiO_2) particle incorporating Au NPs for the system. Because SiO_2 particles are widely known as materials with high colloidal stability, SiO_2 can prevent the Au NPs from agglomeration. In addition, all the surface of the Au NP in the hollow SiO_2 particle is exposed to the liquid phase, therefore the specific properties of the NPs can be efficiently used.

In Chapter 2, previous reports on controlling the assemblies of plasmonic NPs are categorized into static and dynamic controls. The static controls are further categorized as top-down and bottom-up approaches. As for the top-down approaches, lithography techniques such as electron beam lithography, ion beam lithography, and nanosphere lithography are focused on. By contrast, chemical bonds between the NPs and capillary-force driven assembling methods are some of the examples of bottom-up approaches. Employing the statically controlled techniques can achieve precise design of plasmonic assemblies, whereas some expensive experimental equipment is necessary. Compared with the static control methods, the external stimulation of NPs is cost-effective and offers a variety of operational factors to control the assembled states of the NPs. In this chapter, the control of plasmonic NP assemblies via external stimuli such as pH, temperature, light, magnetic field, and electric field are summarized. Among them, an external AC electric field has a potential of diversifying the assembled states of NPs due to a variety of operational factors such as field strength, application frequency, and application time.

Based on the previous reports summarized in Chapter 2, the dynamic control with application of an external AC electric field is employed for reversible control over the spatial distribution of Au NPs. In Chapter 3, the assembling phenomenon of Au NPs in a liquid under application of an AC electric field is investigated. The optical and sensing properties of Au NPs in suspension were measured after the field application with different field conditions. The UV-Vis spectra were altered by the field application, suggesting that the Au NPs formed clusters. In particular, the spectra of Au NPs were broadened by 0.1 kHz field application. The optical properties and the sizes of Au NP assemblies were strongly correlated to each other according to a combined result of the UV-Vis spectra and size distributions measured with a dynamic light scattering (DLS) photometer. Lower Raman intensities were observed for the Au NP suspension treated by field application of a low-frequency of 0.1 kHz in 30 V/mm compared to those without the electric field. The result was probably due to rapid aggregation and sedimentation of Au NPs. Conversely, the field application at high frequencies of 1 kHz or 1 MHz successfully enhanced the Raman intensities by approximately 150%. The assembled states of Au NPs were gradually changed by the high-frequency field application time, suggesting that field application for an appropriate period can be a practical way to control the clustered states of plasmonic NPs. The present results showed that application of an external AC electric field is a promising approach to obtain specific properties from plasmonic NPs in a liquid phase. However, it was not likely that the Au NP clusters formed via the electric field were redispersed in their suspension due to the strong aggregation of Au NPs.

For the reversible control over the spatial distribution of Au NPs, hollow SiO_2 particles incorporating a Au NP are synthesized in Chapter 4. To clarify the relation between the assembled states of the NPs and their sensing property, Au NPs were functionalized with a probe molecule, 4-Mercaptobenzoic Acid (PMBA), before silica coating. The hollow particles incorporating a Au-PMBA NP (Au-PMBA@hSiO_2) are prepared by a selective etching process using polyethylenimine (PEI). The Au-PMBA@hSiO_2 particles were synthesized by the following steps: (1) synthesis of SiO_2 particles incorporating a Au NP (Au-PMBA@SiO_2), (2) modification of the Au-PMBA@SiO_2 with PEI, and (3) etching of the PEI-modified

Au-PMBA@SiO_2 with water. The PEI molecules on SiO_2 surface in water creates a locally basic condition, and protect the surfaces of Au@SiO_2. Only the inner part of Au@SiO_2 particles modified with PEI was gradually etched with water during immersion of Au@SiO_2 in water for 15 h. Spherical hollow particles, however, was deformed by etching them for 18 h or longer. The hollow particles incorporating multiple Au NPs (mAu-PMBA@hSiO_2) are also synthesized. In order to incorporate of multiple Au NPs in a SiO_2 shell, we adjusted the concentration of Au NPs added in the synthetic step for Au-PMBA@SiO_2. The number of Au NPs in the SiO_2 shell was controlled by adjusting the Au NP concentration. The plasmonic properties of the hollow SiO_2 particles depended on the number of Au NPs inside the shell. The extinction peaks of Au-PMBA@hSiO_2 were sharply observed at approximately 530 nm, whereas broad peaks were observed for mAu-PMBA@hSiO_2. Raman intensities of PMBA were dramatically enhanced by incorporating multiple Au NPs into the hollow particle (mAu-PMBA@hSiO_2). This suggested that hotspots were created between Au NPs in the SiO_2 shell compartment.

In Chapter 5, the inner Au NPs in the hollow SiO_2 sphere are focused on. First, the movements of inner Au NPs in the hollow sphere are observed with a liquid cell transmission electron microscopy (LCTEM). The LCTEM observation experimentally showed the movement of a single Au NP in the shell compartment, which suggested that the hollow particle-structure is usable for exposing a whole surface of a Au NP. Multiple Au NPs connected each other in the hollow SiO_2 moved as a Au NP cluster instead of dispersed NPs. Next, the strengths of electric fields induced by incident light are calculated using Maxwell's equation with a finite element method. A maximum strength of the electric field induced in the vicinity of a single Au NP was calculated to 7 V/m, whereas that of Au NP dimer was 700 V/m. The strength of electric fields between Au NPs was increased by increasing the number of Au NPs in the cluster. Formation of Au NP clusters enhanced the calculated maximum field approximately 100 times higher than that of a single Au NP. The numerical results showed that hotspots are created between Au NPs in the SiO_2 shell compartment. Furthermore, the combined result of the LCTEM observation and the numerical result indicated that the hollow particles provide a confined space in which Au NP can form their clusters in order to create hotspots.

The assembled states of Au NPs incorporated into the hollow particles (Au-PMBA@hSiO_2 or mAu-PMBA@hSiO_2) are reversibly controlled via applying an AC electric field in Chapter 6. During the Raman measurement, the external AC field at a frequency of 1 kHz was applied to (m)Au-PMBA@hSiO_2 particle suspensions which were sealed in a glass capillary with electrodes 1 mm apart. The Raman intensities of PMBA were gradually increased during a 50 V/mm field application for 10 min. The Raman intensities were strongly related to the assembled states of the (m)Au-PMBA@hSiO_2 particles in solution. The assembled states of the (m)Au-PMBA@hSiO_2 after application of the electric field were observed with an optical microscope. Although it was difficult to observe a single hollow particle because of the particle sizes much smaller than visible light wavelengths, the local number densities of the particles in a vicinity of electrodes

different from that in a center part of capillary. This experimentally showed that the spatial distribution of the particles was successfully controlled by the electric field. Clear differences of the Raman intensities with and without the electric field were observed more distinctly in the case of mAu-PMBA@hSiO_2 particles compared to those of Au-PMBA@hSiO_2 particles. Raman intensities of PMBA in the presence of the particles were reversibly changed by switching ON and OFF states of the electric field. However, the extinction peaks of the particle suspensions acquired after the field application were almost the same as those without the field application, showing that hotspots for SERS were not created between Au NPs in the shell compartment. The improvement of the sensing properties of the particles indicated that assembling (m)Au-PMBA@hSiO_2 particles with an electric field can be an effective approach to reversibly control the collective properties of plasmonic NPs even if no hotspots are created between the NPs incorporated into different hollow particles.

In Chapter 7, conclusion of the present work is described. In this thesis, we proposed a new system for reversible control over the spatial distribution of Au NPs in a liquid phase. The spatial distribution of Au NPs was successfully controlled using hollow particle structures with the following steps: (i) incorporation of Au NP clusters with the different numbers in hollow SiO_2 particles, and (ii) reversible control over the assembled states of Au NPs incorporated within the hollow particles by switching ON and OFF states of an external AC electric field. The proposed system is applicable to other nano-sized particles which have a low colloidal stability. The system solves the dilemma of agglomeration of particles while they are assembled in a liquid phase, and it possibly leads to enhancement of properties of nanomaterials.